Statistical Thermodynamics in Chemistry and Biology

1. Principles of probability

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Foundations of entropy

Probability and entropy

The reason we have to deal with probability, multiplicity and combinatorics is that it is the foundation of describing entropy.

Definition of entropy, S

In Chapter 6, Boltzmann's law:

$$S = k_B \ln W$$

where k_B is Boltzmann's constant. We have a link between the macroscopic quantity, the entropy, S, and the multiplicity, W, of the microscopic degrees of freedom.

What is probability?

- Let's have in total N trials/events/measurements.
- The outcome of a trial/event/measurement may be A, B, C, etc. In total we have t distinct outcomes.
- n_A, n_B, n_C, etc. are the *number* of outcomes for each category, A, B, C, etc.
- The probability, p_A, of outcome A is

$$p_A = \frac{n_A}{N}$$

where

$$\sum_{J=1}^{t} n_J = N \quad \text{and} \quad \sum_{J=1}^{t} p_J = 1$$

- We will often use its differential form (regard N as a constant)

$$dp_A = \frac{dn_A}{N} \; ; \quad \sum_{J=1}^{t} dn_J = 0 \quad \text{and} \quad \sum_{J=1}^{t} dp_J = 0$$

Simple example: two dice

Let's role two dice. The outcome of each event may be described by a pair of numbers, (a, b), each in the range $1 - 6$.

- What is the probability of the outcome $(6, 6)$? *We have in total* $6 \times 6 = 36$ *possibilities. The probability is thus* $\frac{1}{36} = 0.0278$.
- What is the probability of the outcome $(5, 5)$ or the outcome $(6, 6)$? *It is simply the sum of the probabilities for each outcome:* $\frac{2}{36} = 0.0556$
- What is the probability of the total score 12? What is the probability of getting the total score 11? *: The probability of the total score* 12 *is the same as in the previous question since* $(6, 6)$ *is the only way to obtain* 12. *There are two ways to obtain* 11, $(5, 6)$ *and* $(6, 5)$, *so the probability becomes* $\frac{2}{36}$.

Simple example: two dice

Part 2

- Let's role the dice twice:
  - What is the probability that the first and the second outcomes are $(6, 6)$? *It is simply the product of the probabilities for each outcome:* $\frac{1}{36^2} = 0.00077$
  - What is the probability that the first or the second outcome is $(6, 6)$? *It is easier to calculate one minus the probability for not obtaining* $(6, 6)$ *in the first and second outcome:* $p = 1 - \left(\frac{35}{36}\right)^2 = 0.0548$
  - What are the limiting values, $N \rightarrow \infty$, if we repeat the event N times? *The probability to get* $(6, 6)$ *in each event approaches zero for large* N. *The probability to get* $(6, 6)$ *once approaches one for large* N.

Second example: multiplicity

- N identical, non-interacting particles (molecules)
- Each particle has discrete energy states, ε_i, given by the Schrödinger equation in quantum mechanics: $\hat{H}\psi_i = \varepsilon_i\psi_i$
- The total energy, E, is given as a constraint
- We have
  - n_0 particles with energy ε_0 on level 0,
  - n_1 particles with energy ε_1 on level 1, etc.
- We get (as a sum over all states)

$$N = \sum_{i=0}^{\infty} n_i \; ; \qquad E = \sum_{i=0}^{\infty} \varepsilon_i n_i$$

- Example: $E = N\varepsilon_0$ (all particles in the ground state)
- For E larger than $N\varepsilon_0$: many possibilities

Second example: multiplicity

Part 2

Simple question

In how many different ways can we put n_0 particles on level 0, n_1 particles on level 1, etc.?

- Example: $N = 12$, $n_0 = 5$, $n_1 = 4$, $n_2 = 2$, $n_3 = 1$
- We start by choosing particles at level 0:
  - First particle: N possibilities,
  - Second particle: $N - 1$ possibilities, etc.
  - Total number of possibilities: $N(N-1)(N-2)(N-3)(N-4)$
  - This is correct if the particles are distinguishable
  - If indistinguishable: 5! identical combinations.
  - Total number of possibilities:

$$\frac{N(N-1)(N-2)(N-3)(N-4)}{5!}$$

Second example: multiplicity

Part 3

- For $n_0 = 5$,
$$\frac{N(N-1)(N-2)(N-3)(N-4)}{5!}$$
- For $n_1 = 4$,
$$\frac{(N-5)(N-6)(N-7)(N-8)}{4!}$$
- For $n_2 = 2$,
$$\frac{(N-9)(N-10)}{2!}$$
- For $n_3 = 1$,
$$\frac{(N-11)}{1!}$$
- The total number of combinations, Ω, (the multinominial distribution),
$$\Omega = \frac{N!}{(n_0!)(n_1!)(n_2!)(n_3!)} = \frac{N!}{\prod_i n_i!}$$
which we also denote the multiplicity, W.

Third example

- Constraint: Total energy, $E = 4\varepsilon$, is constant
- Model system: 4 molecules in three energy levels: ε_0, ε_1, and ε_2.
- Equidistant energy levels: $\varepsilon_0 = 0$, $\varepsilon_1 = \varepsilon$, $\varepsilon_2 = 2\varepsilon$
- Three ways to fulfill the constraints, $E = 4\varepsilon$ and $N = 4$:
  - $2\epsilon_2 + 2\epsilon_0$
  - $\epsilon_2 + 2\epsilon_1 + \epsilon_0$,
  - $4\epsilon_1$,
- We get the multiplicities,

$$W_1 = \frac{N!}{\prod_i n_i!} = \frac{4!}{2!0!2!} = 6$$

$$W_2 = \frac{N!}{\prod_i n_i!} = \frac{4!}{1!2!1!} = 12$$

$$W_3 = \frac{N!}{\prod_i n_i!} = \frac{4!}{0!4!0!} = 1$$

- Which one is most common? Entropy? Which one do we regard as most unordered?

First example of lattice model

- Regard a surface where molecules A and B are placed on a surface: $n_A = 20$, $n_B = 20$, $N = n_A + n_B$.
- Regard two cases: We put a label on each molecule (left), and we only label them by the type of molecule A and B (right).

A_9	B_3	B_{12}	B_2	A_{13}	A_5	B_{11}	B_4
B_1	A_{12}	B_{14}	A_{10}	B_{15}	A_6	A_{16}	B_{13}
B_{17}	A_8	A_2	B_9	A_{14}	B_{16}	A_{15}	A_4
A_{20}	A_7	A_{18}	B_{18}	B_7	A_{19}	B_{19}	B_8
A_1	B_5	B_{10}	A_{11}	A_{17}	B_{20}	A_3	B_6

A	B	B	B	A	A	B	B
B	A	B	A	B	A	A	B
B	A	A	B	A	B	A	A
A	A	A	B	B	A	B	B
A	B	B	A	A	B	A	B

- Left: $W = N!$ Right: $W = \frac{N!}{n_A! n_B!}$
- The ”right” case will be used all the time for molecular systems.

Summary

- Discussed probability
- Introduction to combinatorics to give the multiplicity
- Not discussed (but used later): average, variance, etc.
- Some questions for thought:
  - What happens if we put two objects with different temperature in contact?
  - What happens if we put a drop of ink in water?
  - Can we understand this behaviour already now?